

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 761 755 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
12.03.1997 Bulletin 1997/11

(51) Int. Cl.⁶: **C08L 23/28**, C09K 21/14,
C08K 11/00

(21) Application number: 96201895.8

(22) Date of filing: 08.07.1996

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 21.08.1995 US 515083

(71) Applicant: **GENERAL MOTORS CORPORATION**
Detroit Michigan 48202 (US)

(72) Inventors:
• **Abu-Isa, Ismat Ali**
Rochester Hills, Michigan 48309 (US)

• **Jaynes, Craig Bryant**
Bloomfield Hills, Michigan 48302 (US)

(74) Representative: **Denton, Michael John et al**
Patent Section
1st Floor
Gideon House
28 Chapel Street
Luton Bedfordshire LU1 2SE (GB)

(54) **Moldable intumescent thermoplastic compositions**

(57) An intumescent thermoplastic molding composition is disclosed that includes a moldable thermoplastic chlorinated polymer consisting of chlorinated polyethylene elastomer or mixtures of chlorinated polyethylene elastomer with at least one of polyvinyl chloride and high density polyethylene; a heat stabilizer for the thermoplastic chlorinated polymer material and an intumescent and fire-resistant additive for the chlorinated polymer material, whereby moldings prepared from such mixture have good physical properties over a substantial range of ambient temperatures and display a resistance to flame and heat as characterized by the Intumescence Efficiency test of this specification.

EP 0 761 755 A1

DescriptionTechnical Field

5 This invention relates to moldable intumescent thermoplastic compositions that have certain minimal physical properties and an intumescent efficiency as determined by tests described in the specification such that the moldable compositions are useful over a wide range of ambient temperatures and hydrocarbon-containing environments and the like.

Background of the Invention

10 Intumescent paints have been devised for use on wall surfaces of buildings, ships or other structures or vessels intended for human occupancy and which are susceptible to fires. Intumescent coatings contain ingredients which will react on severe heating to generate gases and form an incombustible or low combustible residue. The expelled gases expand the residue into a thin foam layer with thermal insulating properties. The foam produced from the coating must
 15 be tough and adherent so as to resist violent drafts and thermal expansion forces arising from the fire. In many instances, the residue is a carbon char which is formed by the dehydration of a polyhydric substance such as a polyalcohol. The reactions all take place within the coating so when the coating film is heated to beyond a specific elevated temperature, an intumescent additive such as the polyhydric alcohol is decomposed, generating water, carbon dioxide, ammonia and/or other heat absorbing gases that do not readily support combustion.

20 While intumescent coatings have been available, they are not always easy to apply where needed and they can serve no purpose other than as a coating. It would be desirable to provide a group of moldable thermoplastic compositions having intumescent properties. Such moldable thermoplastic compositions could be shaped into any desired configuration at a suitable manufacturing location and serve a useful purpose such as a structural member, a shelf or other storage member, or a sound-deadening or other barrier member in addition to providing an intumescent barrier in the
 25 event of a fire. Heretofore, such moldable intumescent thermoplastic compositions have not been available, especially compositions possessing suitable physical properties over a range of ambient temperatures such as might be experienced in a ship or an automobile or the like.

Summary of the Invention

30 This invention comprises a family of new thermoplastic molding compositions that provide intumescent properties to moldings formed from them. Moreover, moldings produced from the compositions suitably have at least certain minimal physical properties such as a tensile strength of 2.7 MPa (400 psi) and an elongation at break of at least 50 percent at normal room temperature (ASTM D412). Such properties give moldings sufficient strength and durability so as to be
 35 useful in architectural applications, automotive applications, marine applications or the like. In addition to having useful physical properties for such applications, the moldings also have "intumescence efficiency." When exposed to elevated temperatures, the intumescent additives react or decompose to convert the molded plastic body to a residual insulating foam-like structure that is resistant to burning and insulates the back side of the molding from the high temperatures of the combustion flame.

40 Suitable constituents of the subject intumescent thermoplastic molding compositions comprise a moldable chlorinated polymer material which may be solely a suitable chlorinated polyethylene elastomer or a mixture of such elastomer(s) with one or more thermoplastic polymers such as polyvinyl chloride and/or high density polyethylene. Usually the chlorinated polyethylene elastomer will constitute more than 25 percent of the elastomer resin/thermoplastic resin mixture, and as stated, the chlorinated polyethylene may be the sole polymeric constituent of the molding material.

45 A second constituent of the moldable intumescent material is a heat stabilizer which protects the molding compositions against thermal degradation during formulation and molding and further contributes to the ability of the compositions to resist ignition and heat transfer at high temperatures. Suitably, the heat stabilizer additive(s) will constitute about 5 to 15 percent by weight of the total of the chlorinated polymer mixture plus heat stabilizer. Examples of suitable heat stabilizers are magnesium oxide, hydroquinone derivatives, organic phosphite heat stabilizers such as tetraphenyl
 50 dipropylene glycol diphosphate (THOP, a product of General Electric Specialty Chemicals), hindered phenols such as the Irganox group of known heat stabilizers supplied by Ciba-Geigy Company, e.g., tetrakis [methylene-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate] methane, amine antioxidants and thio esters such as distearylthiodipropionate (DSTDTP).

55 A third essential ingredient of the moldable chlorinated polymer formulation of this invention is, of course, the intumescent additives. Such additives are frequently used in combination so as to provide a variety of volatile heat-consuming and foam-forming gaseous emissions. Examples of suitable intumescent additives include antimony trioxide, ammonium dihydrogen phosphate, corn starch, hydrated alumina and like materials with a plurality of hydroxyl groups. Examples of other polyhydroxy intumescent materials include sugars (carbohydrates), tetrahydroxy compounds such as pentaerythritol and trihydroxy compounds such as trimethylol propane. Suitably, the intumescent additive(s) make

up about 25 to 40 percent by weight of the total weight of chlorinated polymer mixture and intumescent additives.

While a variety of the heat stabilizers and intumescent additives are known from other technologies such as the intumescent coating technology or conventional thermoplastic molding technology, the selection of the specific additives employed in each instance will be such as to be compatible with the chlorinated polymer materials employed to provide the physical properties and intumescent efficiency properties of the subject molding compounds.

In addition to the above essential ingredients, plasticizers may be incorporated in the material to provide low temperature impact resistance and flexibility imparting properties. Also, reinforcing materials such as 3/16-inch glass fibers or the like may be employed to provide higher tensile strength and other physical properties of such reinforced composites. However, in accordance with this invention, the essential ingredients and any additional ingredients are balanced in the overall formulation to provide thermoplastic moldings having a minimal tensile strength of 2.7 megapascals (MPa, or about 400 pounds force per square inch) and a minimum elongation at break of 50 percent in combination with an intumescence efficiency of no more than 450°C as determined hereinbelow.

Further advantages of the invention will be more apparent from a detailed description thereof which follows. Reference will be had to the drawings.

Brief Description of the Drawings

Figure 1 is a perspective view of apparatus for measuring the efficiency of intumescent moldable compositions in accordance with this invention.

Figure 2 is a graph depicting temperature versus time at different locations of a steel plate protected by a molded intumescent composition in accordance with the invention.

Figure 3 is a graph of stress versus strain of a formulation prepared in accordance with the invention.

Figure 4 is a graph depicting a thermogravimetric analysis of an intumescent material prepared in accordance with the invention.

Description of an Embodiment of the Invention

This invention provides intumescent thermoplastic molding compositions that can be blow molded, injection molded, compression molded or otherwise suitably molded and shaped to a desired geometry or configuration by thermal processes. The molded part may be intended to serve primarily as a heat or fire barrier. More often, it will also serve another purpose and serve incidentally as a heat or fire barrier. In either case, the invention provides a moldable material that can be formed in a suitable manufacturing facility and transported for efficient handling at an automobile assembly line or at a construction site or the like. Thus, the subject composition facilitates efficient manufacture and assembly and provides robust physical and fire-resistant properties in use.

The polymeric constituent of this invention includes a chlorinated polyethylene elastomer(s) or a thermoplastic elastomer mixture composed of chlorinated polyethylene as the soft elastomeric phase and one or both thermoplastic polymeric resins selected from the group consisting of polyvinyl chloride and high density polyethylene as the included and distributed hard phase. The elastomer portion of the composition can be used with or without a small amount of crosslinking agent provided that the overall composition can be processed thermoplastically. The essential ingredients of the formulation include such thermoplastic elastomer mixture or chlorinated polyethylene elastomer alone, together with a suitable heat stabilizer composition and content as well as suitable intumescence and fire resistance additives and content. The identity of suitable heat stabilizers has been summarized above, as has the identity of a small number of suitable intumescent and fire resistance providing additives. The usage of these materials will be further illustrated in the specific examples which follow.

In addition to the essential polymer content and heat stabilizer and intumescence additives, certain other materials are suitable optional constituents. Glass fiber or other fibrous or particulate reinforcing material may be employed to increase mechanical and thermal properties of the molded composition when an application requires such properties. In addition, there will be product applications such as those for low temperature usage in which plasticizers may be incorporated into the moldable compositions. In general, two types of plasticizers have been demonstrated to achieve good low temperature properties. They include liquid chlorowax-type plasticizers and the liquid organic phosphate or ester-type plasticizers. Again, specific examples of these materials will be illustrated in the examples that follow.

The following Table 1 summarizes eight specific compositions of chlorinated polyethylene (CPE, Tyrin 4211P) and mixtures of this CPE with polyvinyl chloride PVC (Geon 179). Tyrin 4211P is a trademark of the Dow Chemical Company. This resin contains 42 percent by weight chlorine, has an ultimate elongation (ASTM D412) of 500 percent, a tensile strength (ASTM D412) of 126.7 kg/cm² (1800 psi) and a 100 percent modulus (ASTM D412) of 17.6 kg/cm² (250 psi). Other CPE elastomeric resins may be used. It is preferred that they have a chlorine content of about 36 to 42 percent and that they have comparable physical properties. Geon 179 is a trademark of the Geon Company, and this unplasticized powdered resin is characterized by a small average particle size of 0.56 to 1.6 microns and a low gel temperature of 66°C to 96°C. Such small particle size PVC is preferred because it readily incorporates a plasticizer when

one is employed.

The values in Table 1 opposite each ingredient are parts by weight, and the numbers for each composition total 100.

TABLE 1

Ingredients	Compositions							
	1	2	3	4	5	6	7	8
Chlorinated Polyethylene CPE (Tyrin 4211P)	60	57	40	40	31	37	33	33
Polyvinyl Chloride PVC (Geon 179)	--	14	31	30	23	27	25	25
Chlorowax 70S	6	--	--	--	--	--	--	--
Magnesium Oxide	8	4	4	4	3	4	3	3
THOP Phosphite	1	--	--	1	1	1	1	1
Irganox 1010 Antioxidant	1	1	1	1	1	1	1	1
Antimony Trioxide	8	8	8	8	6	7	7	7
Ammonium Dihydrogen Phosphate	9	9	9	9	7	8	8	8
Corn Starch	7	7	7	7	5	6	6	6
3/16 Chopped Glass (183G)	--	--	--	--	23	9	8	--
Hydrated Alumina	--	--	--	--	--	--	8	16
Intumescence Efficiency, °C	425	292	282	353	353	309	301	329

The above eight compositions were prepared, mixed and molded and tested for certain physical and intumescence properties as follows.

Mixing of the Compositions

The mixing of compositions described herein on a laboratory scale was achieved by different methods including mixing on a two-roll mill heated to 65°C. The polymeric resin or resins and the stabilizers were added to the rolls and shear mixed for about five minutes. At that time good mixing was visually observed and the material was banded on one of the rolls. The actual temperature of the resin during mixing approached 150°C due to shearing of the mixture. The ingredients for intumescence were added next. They were added in a fine powder form and mixed well with the resin. In compositions 5, 6 and 7, glass fibers were then added and mixed into the formulation for about three minutes. The total mixing time of each compound was about 15 minutes.

In alternative practices, formulations were also prepared by mixing in a Brabender bowl, which is a small internal mixer, and in a large Banbury internal mixer. In these practices, for example, the Banbury cavity is preheated to 93°C. Then, a first batch of ingredients is added to the bowl. These ingredients include (for example) chlorinated polyethylene and polyethylene, magnesium oxide, hydrated alumina, DSTDP, antimony oxide, corn starch and chlorowax. The mixing speed of the bowl was then increased to 120 rpm, and the ingredients were allowed to mix for two to three minutes. In this example utilizing polyethylene, the temperature of the mix was permitted to rise above about 120°C to melt the polyethylene and incorporate it into the mixture but not permitted to rise above 140°C to ensure that the products did not undergo degradation. Following this first mixing operation, a second batch of ingredients which include, for example, ammonium dihydrogen phosphate, melamine and glass were added to the bowl, mixing was continued for three more minutes or until the temperature reached about 160°C, whichever first occurred. The mix was then removed from the bowl and dumped onto a mill to further mix and sheet out the composition. The temperature of the mill in the case of this example was about 132°C.

Another example of resin composition mixing that is suitable with the subject moldable compositions involves a Brabender extruder. The effect of temperature and shear rate has been investigated with this extruding device. The temperatures of the three extruder barrel zones and the die were all varied between 150°C and 175°C. Three settings of the screw speeds were investigated, namely 50, 75 and 100 rpm. The length-to-diameter ratio of the screw was 20 to 1, and the compression ratio was 1. The material extruded well and exhibited good mixing at all of the above conditions. Large scale batches were prepared using a twin screw Buss kneader.

Molding Example

Portions of each of the above mixed compositions 1 through 8 from Table 1 were prepared in the form of molded slabs using compression molds and a heated press. The slabs were square (152 mm by 152 mm) and were molded with thicknesses in the range of 0.2 mm to 2.75 mm. Other types of thermoplastic molding operations such as injection molding, vacuum forming and blow molding may also be utilized to prepare suitable molded structures in accordance with this invention.

Intumescent Test Apparatus

All of the moldable compositions illustrated in this specification have been tested as intumescent compositions to be used for resisting the spread of a flame from a fire source and curtailing temperature rise. The characteristic or property of Intumescence Efficiency as ascribed to moldings from the subject compositions were determined in an apparatus and by a practice as follows. When reference is made to such property in this specification or claims, it is intended that the property be determined utilizing such an apparatus or the equivalent and such practices.

The Intumescence Efficiency test apparatus is shown in Figure 1. Apparatus 10 included a three-wall steel chamber comprising left side wall 12, back wall 14 and right side wall 16. Each wall was a steel plate 229 mm high, 127 mm wide and 1 mm thick. The plates were joined at their edges as shown in Figure 1 to form a generally square-shaped (in cross section) chamber with an open front.

A 152 mm by 152 mm by 1 mm thick steel plate adapted to be placed on top of walls 12, 14 and 16 was employed as a roof member 18. During a test, the roof member 18 carried affixed to its lower surface a molded 127 mm x 152 mm x 2.75 mm rectangular molded slab 20 of material to be tested for Intumescence Efficiency. Note that the thickness of 2.75 mm of the test specimen (as well as its composition) is important to the repeatability of this test. As shown, the intumescent slab 20 faces downward inside of the roof 18 and chamber during the test. On the top surface 22 of the steel roof panel 18 were located six thermocouple leads in the locations indicated, respectively 101, 102, 103, 104, 105 and 106.

A 165 mm tall Bunsen burner 24 was used as the flame source. The height of the burner did not include the flame height. The flame height was of the order of 60 mm, and it was adjusted during each test so that the tip of the inner blue cone of the flame 25, its hottest part, touched the surface of the intumescent material. A thermocouple indicated at 26 was placed at the lower surface of the intumescent coating 20 to measure the flame temperature as it impinged on the intumescent material at that point. The flame temperature as measured by thermocouple 26 was at a location on the intumescent material opposite the location of thermocouple 104 on the top surface 22 of the steel roof member 18.

While six thermocouple locations as indicated in Figure 1 were initially used in testing of intumescence efficiency, experience has shown that equivalent useful data is obtained from using only four thermocouples at locations 101, 102, 104 and 106.

Evaluation of the Formulations

A molded slab of formulation 1 (referring to Table 1) was exposed to the flame of the Bunsen burner in the test apparatus 10. Figure 2 is a graph of temperature (in degrees Celsius) versus time (in minutes) of the thermocouple measured temperatures at locations 101-106 on the top surface 22 of steel plate 24 protected by intumescent material 20 of formulation 1. The curve for the flame temperature in Figure 2 is designated 110. The curves for the other thermocouple readings in Figure 2 are designated with the number of their thermocouple location.

The flame temperature shot up to over 1000°C within one-half minute and then decreased somewhat as the cooling effect of the gas evolution of the intumescent material in formulation 1 was seen in the flame temperature. However, after a period of about four minutes, the flame temperature again levelled off at 1000°C. The molded formulation 1 slab, which was based on CPE resin, displayed no sign of dripping or burning when exposed to the direct flame and heated drastically. The sample was heated for 30 minutes. It charred and swelled to a thickness greater than its original thickness when it was exposed to the flame. It is seen that as the respective thermocouples reach an equilibrium temperature, thermocouple 104 consistently recorded the highest temperature. This maximum temperature was 425°C. Thermocouple locations 101 and 106 were the lowest temperatures, while the plotted temperatures for thermocouple locations 102, 103 and 105 were so close as to be virtually indistinguishable. The highest temperature recorded on the top side of the steel roof of apparatus 10 is taken as the "Intumescence Efficiency" for its formulation 1 molded slab. This temperature, i.e. the Intumescence Efficiency, as noted above was 425°C.

In general, it is observed that unless the test material ignites, the maximum temperature that is recorded by a thermocouple on the roof member of the test apparatus is at location 104 because that location is immediately above the flame of the Bunsen burner.

Each of the other formulations described in this specification were tested as molded slabs of the same dimensions in the same test apparatus and by the 30-minute flame heating practice identical to that described above. Recordings

of flame temperature and thermocouple temperatures were made similar to that depicted in Figure 2 with respect to the composition 1 molded slab. While the closeness or the spread of the thermocouple temperatures varied from test to test, in each instance the maximum temperature following the decomposition of the intumescent additives in the molding was taken as the measure of Intumescence Efficiency. The highest temperature, in degrees Celsius, is reported as Intumescence Efficiency for each of compositions 1 through 8 in Table 1.

Composition 2 was the first of the formulations illustrated that contained polyvinyl chloride in combination with chlorinated polyethylene. When this formulation was subjected to the intumescence efficiency test in apparatus 10, it did not drip or ignite. Again, the slab sample simply charred and swelled into an insulating blanket as expected for a suitable intumescent material when it was exposed to the flame. However, in this instance, the maximum temperature measured on the steel roof during the 30 minute test was only 291°C. Hence, this composition is more effective in terms of Intumescent Efficiency than composition 1. Compositions 3 and 4 are like composition 2 but with higher concentrations of polyvinyl chloride. Addition of higher concentrations of polyvinyl chloride leads to higher modulus and better handling characteristics in the mixing and the preparation of the product. Glass fiber was introduced in formulations 5 and 6. The fibrous glass reinforcement gives these formulations higher stiffness, and the Intumescence Efficiency testing showed that the presence of glass in the material did not diminish its effectiveness as an intumescent material.

All of the compositions 1 through 8 were exposed to the Bunsen burner flame for 45 minutes even though the test was viewed as completed at 30 minutes. In each composition sample, initial burning and charring of the resin component was observed but the samples did not sustain combustion. Each sample expanded to form an insulating blanket having a thickness larger than that of the original molding. In the intumescent condition, they maintained their shape well and surprisingly exhibited strength and some structural integrity. In other words, they did not crumble or flake off the roof member 18 of apparatus 10. They formed a ceramic blanket which upon analysis is found to consist of glass, carbon, phosphorus, alumina and magnesia.

Samples with lower glass concentrations appeared to perform better in terms of thermal insulation.

A number of molded test specimens of the formulation containing fiberglass and hydrated alumina (composition 7 of Table 1) were used to produce the following data. An average stress/strain curve of five samples of glass fiber-filled composition 7 is shown in Figure 3. The ultimate tensile strength is 13 MPa, and the ultimate elongation is 75 percent as measured per ASTM D638. The die C tear strength of the material was measured per ASTM D624 and found to have an average value of 48 kN/M. The flexural modulus was measured per ASTM D790 and found to be 460 MPa. All measurements were conducted at room temperature.

The effect of temperature on the molded composition 7 is illustrated using thermogravimetric analysis (TGA). The TGA data in air for composition 7 is depicted in Figure 4. It shows that no appreciable degradation of the intumescent molded slab occurs below 200°C.

Solvent Resistance of Formulation 1

In automotive applications and in other applications where the molded compositions of this invention are exposed to a range of solvents, it is important to know the resistance of the coating to such materials. The results of the effect of different automotive fluids on the degree of swell and tear strength of molded specimens of composition 1 are shown in Table 2. The percentage swell in water, windshield fluid, salt water and coolant were all less than one percent, whereas the swell in transmission fluid was 1.2 percent and in brake fluid 2.3 percent. The tear strength results of all samples after exposure to the fluids for at least four hours at room temperature were all within six percent of tear strength value of the unexposed control sample.

TABLE 2

Automotive Fluid Resistance of Intumescent Coating (Composition 1 of Table 1)		
Fluid	% Swell	Tear Strength (kN/M)
None	--	32.7
Water	0.49	32.7
Salt Water	0.22	34.8
Transmission Fluid	1.20	31.9
Windshield Fluid	-0.16	31.7
Brake Fluid	2.30	33.5
Coolant	-0.12	32.7

Plasticizer Additions

The above-described eight illustrative compositions of this invention were essentially unplasticized. In order to increase the utility of the subject moldable intumescent compositions to a wider range of applications and of processing methods, the influence of plasticizers on the properties of the basic compositions were investigated. The plasticizers investigated were isodecyl diphenyl phosphate (Santicizer 141, a trademark of Monsanto Company), 2 ethylhexyl diphenyl phosphate (Santicizer 148, Monsanto), butylbenzyl phthalate (Santicizer 170, Monsanto), and chlorowax (Par-
 10
 15
 20
 25
 30
 35
 40
 45
 50
 55
 60
 65
 70
 75
 80
 85
 90
 95
 100
 105
 110
 115
 120
 125
 130
 135
 140
 145
 150
 155
 160
 165
 170
 175
 180
 185
 190
 195
 200
 205
 210
 215
 220
 225
 230
 235
 240
 245
 250
 255
 260
 265
 270
 275
 280
 285
 290
 295
 300
 305
 310
 315
 320
 325
 330
 335
 340
 345
 350
 355
 360
 365
 370
 375
 380
 385
 390
 395
 400
 405
 410
 415
 420
 425
 430
 435
 440
 445
 450
 455
 460
 465
 470
 475
 480
 485
 490
 495
 500
 505
 510
 515
 520
 525
 530
 535
 540
 545
 550
 555
 560
 565
 570
 575
 580
 585
 590
 595
 600
 605
 610
 615
 620
 625
 630
 635
 640
 645
 650
 655
 660
 665
 670
 675
 680
 685
 690
 695
 700
 705
 710
 715
 720
 725
 730
 735
 740
 745
 750
 755
 760
 765
 770
 775
 780
 785
 790
 795
 800
 805
 810
 815
 820
 825
 830
 835
 840
 845
 850
 855
 860
 865
 870
 875
 880
 885
 890
 895
 900
 905
 910
 915
 920
 925
 930
 935
 940
 945
 950
 955
 960
 965
 970
 975
 980
 985
 990
 995
 1000
 1005
 1010
 1015
 1020
 1025
 1030
 1035
 1040
 1045
 1050
 1055
 1060
 1065
 1070
 1075
 1080
 1085
 1090
 1095
 1100
 1105
 1110
 1115
 1120
 1125
 1130
 1135
 1140
 1145
 1150
 1155
 1160
 1165
 1170
 1175
 1180
 1185
 1190
 1195
 1200
 1205
 1210
 1215
 1220
 1225
 1230
 1235
 1240
 1245
 1250
 1255
 1260
 1265
 1270
 1275
 1280
 1285
 1290
 1295
 1300
 1305
 1310
 1315
 1320
 1325
 1330
 1335
 1340
 1345
 1350
 1355
 1360
 1365
 1370
 1375
 1380
 1385
 1390
 1395
 1400
 1405
 1410
 1415
 1420
 1425
 1430
 1435
 1440
 1445
 1450
 1455
 1460
 1465
 1470
 1475
 1480
 1485
 1490
 1495
 1500
 1505
 1510
 1515
 1520
 1525
 1530
 1535
 1540
 1545
 1550
 1555
 1560
 1565
 1570
 1575
 1580
 1585
 1590
 1595
 1600
 1605
 1610
 1615
 1620
 1625
 1630
 1635
 1640
 1645
 1650
 1655
 1660
 1665
 1670
 1675
 1680
 1685
 1690
 1695
 1700
 1705
 1710
 1715
 1720
 1725
 1730
 1735
 1740
 1745
 1750
 1755
 1760
 1765
 1770
 1775
 1780
 1785
 1790
 1795
 1800
 1805
 1810
 1815
 1820
 1825
 1830
 1835
 1840
 1845
 1850
 1855
 1860
 1865
 1870
 1875
 1880
 1885
 1890
 1895
 1900
 1905
 1910
 1915
 1920
 1925
 1930
 1935
 1940
 1945
 1950
 1955
 1960
 1965
 1970
 1975
 1980
 1985
 1990
 1995
 2000
 2005
 2010
 2015
 2020
 2025
 2030
 2035
 2040
 2045
 2050
 2055
 2060
 2065
 2070
 2075
 2080
 2085
 2090
 2095
 2100
 2105
 2110
 2115
 2120
 2125
 2130
 2135
 2140
 2145
 2150
 2155
 2160
 2165
 2170
 2175
 2180
 2185
 2190
 2195
 2200
 2205
 2210
 2215
 2220
 2225
 2230
 2235
 2240
 2245
 2250
 2255
 2260
 2265
 2270
 2275
 2280
 2285
 2290
 2295
 2300
 2305
 2310
 2315
 2320
 2325
 2330
 2335
 2340
 2345
 2350
 2355
 2360
 2365
 2370
 2375
 2380
 2385
 2390
 2395
 2400
 2405
 2410
 2415
 2420
 2425
 2430
 2435
 2440
 2445
 2450
 2455
 2460
 2465
 2470
 2475
 2480
 2485
 2490
 2495
 2500
 2505
 2510
 2515
 2520
 2525
 2530
 2535
 2540
 2545
 2550
 2555
 2560
 2565
 2570
 2575
 2580
 2585
 2590
 2595
 2600
 2605
 2610
 2615
 2620
 2625
 2630
 2635
 2640
 2645
 2650
 2655
 2660
 2665
 2670
 2675
 2680
 2685
 2690
 2695
 2700
 2705
 2710
 2715
 2720
 2725
 2730
 2735
 2740
 2745
 2750
 2755
 2760
 2765
 2770
 2775
 2780
 2785
 2790
 2795
 2800
 2805
 2810
 2815
 2820
 2825
 2830
 2835
 2840
 2845
 2850
 2855
 2860
 2865
 2870
 2875
 2880
 2885
 2890
 2895
 2900
 2905
 2910
 2915
 2920
 2925
 2930
 2935
 2940
 2945
 2950
 2955
 2960
 2965
 2970
 2975
 2980
 2985
 2990
 2995
 3000
 3005
 3010
 3015
 3020
 3025
 3030
 3035
 3040
 3045
 3050
 3055
 3060
 3065
 3070
 3075
 3080
 3085
 3090
 3095
 3100
 3105
 3110
 3115
 3120
 3125
 3130
 3135
 3140
 3145
 3150
 3155
 3160
 3165
 3170
 3175
 3180
 3185
 3190
 3195
 3200
 3205
 3210
 3215
 3220
 3225
 3230
 3235
 3240
 3245
 3250
 3255
 3260
 3265
 3270
 3275
 3280
 3285
 3290
 3295
 3300
 3305
 3310
 3315
 3320
 3325
 3330
 3335
 3340
 3345
 3350
 3355
 3360
 3365
 3370
 3375
 3380
 3385
 3390
 3395
 3400
 3405
 3410
 3415
 3420
 3425
 3430
 3435
 3440
 3445
 3450
 3455
 3460
 3465
 3470
 3475
 3480
 3485
 3490
 3495
 3500
 3505
 3510
 3515
 3520
 3525
 3530
 3535
 3540
 3545
 3550
 3555
 3560
 3565
 3570
 3575
 3580
 3585
 3590
 3595
 3600
 3605
 3610
 3615
 3620
 3625
 3630
 3635
 3640
 3645
 3650
 3655
 3660
 3665
 3670
 3675
 3680
 3685
 3690
 3695
 3700
 3705
 3710
 3715
 3720
 3725
 3730
 3735
 3740
 3745
 3750
 3755
 3760
 3765
 3770
 3775
 3780
 3785
 3790
 3795
 3800
 3805
 3810
 3815
 3820
 3825
 3830
 3835
 3840
 3845
 3850
 3855
 3860
 3865
 3870
 3875
 3880
 3885
 3890
 3895
 3900
 3905
 3910
 3915
 3920
 3925
 3930
 3935
 3940
 3945
 3950
 3955
 3960
 3965
 3970
 3975
 3980
 3985
 3990
 3995
 4000
 4005
 4010
 4015
 4020
 4025
 4030
 4035
 4040
 4045
 4050
 4055
 4060
 4065
 4070
 4075
 4080
 4085
 4090
 4095
 4100
 4105
 4110
 4115
 4120
 4125
 4130
 4135
 4140
 4145
 4150
 4155
 4160
 4165
 4170
 4175
 4180
 4185
 4190
 4195
 4200
 4205
 4210
 4215
 4220
 4225
 4230
 4235
 4240
 4245
 4250
 4255
 4260
 4265
 4270
 4275
 4280
 4285
 4290
 4295
 4300
 4305
 4310
 4315
 4320
 4325
 4330
 4335
 4340
 4345
 4350
 4355
 4360
 4365
 4370
 4375
 4380
 4385
 4390
 4395
 4400
 4405
 4410
 4415
 4420
 4425
 4430
 4435
 4440
 4445
 4450
 4455
 4460
 4465
 4470
 4475
 4480
 4485
 4490
 4495
 4500
 4505
 4510
 4515
 4520
 4525
 4530
 4535
 4540
 4545
 4550
 4555
 4560
 4565
 4570
 4575
 4580
 4585
 4590
 4595
 4600
 4605
 4610
 4615
 4620
 4625
 4630
 4635
 4640
 4645
 4650
 4655
 4660
 4665
 4670
 4675
 4680
 4685
 4690
 4695
 4700
 4705
 4710
 4715
 4720
 4725
 4730
 4735
 4740
 4745
 4750
 4755
 4760
 4765
 4770
 4775
 4780
 4785
 4790
 4795
 4800
 4805
 4810
 4815
 4820
 4825
 4830
 4835
 4840
 4845
 4850
 4855
 4860
 4865
 4870
 4875
 4880
 4885
 4890
 4895
 4900
 4905
 4910
 4915
 4920
 4925
 4930
 4935
 4940
 4945
 4950
 4955
 4960
 4965
 4970
 4975
 4980
 4985
 4990
 4995
 5000
 5005
 5010
 5015
 5020
 5025
 5030
 5035
 5040
 5045
 5050
 5055
 5060
 5065
 5070
 5075
 5080
 5085
 5090
 5095
 5100
 5105
 5110
 5115
 5120
 5125
 5130
 5135
 5140
 5145
 5150
 5155
 5160
 5165
 5170
 5175
 5180
 5185
 5190
 5195
 5200
 5205
 5210
 5215
 5220
 5225
 5230
 5235
 5240
 5245
 5250
 5255
 5260
 5265
 5270
 5275
 5280
 5285
 5290
 5295
 5300
 5305
 5310
 5315
 5320
 5325
 5330
 5335
 5340
 5345
 5350
 5355
 5360
 5365
 5370
 5375
 5380
 5385
 5390
 5395
 5400
 5405
 5410
 5415
 5420
 5425
 5430
 5435
 5440
 5445
 5450
 5455
 5460
 5465
 5470
 5475
 5480
 5485
 5490
 5495
 5500
 5505
 5510
 5515
 5520
 5525
 5530
 5535
 5540
 5545
 5550
 5555
 5560
 5565
 5570
 5575
 5580
 5585
 5590
 5595
 5600
 5605
 5610
 5615
 5620
 5625
 5630
 5635
 5640
 5645
 5650
 5655
 5660
 5665
 5670
 5675
 5680
 5685
 5690
 5695
 5700
 5705
 5710
 5715
 5720
 5725
 5730
 5735
 5740
 5745
 5750
 5755
 5760
 5765
 5770
 5775
 5780
 5785
 5790
 5795
 5800
 5805
 5810
 5815
 5820
 5825
 5830
 5835
 5840
 5845
 5850
 5855
 5860
 5865
 5870
 5875
 5880
 5885
 5890
 5895
 5900
 5905
 5910
 5915
 5920
 5925
 5930
 5935
 5940
 5945
 5950
 5955
 5960
 5965
 5970
 5975
 5980
 5985
 5990
 5995
 6000
 6005
 6010
 6015
 6020
 6025
 6030
 6035
 6040
 6045
 6050
 6055
 6060
 6065
 6070
 6075
 6080
 6085
 6090
 6095
 6100
 6105
 6110
 6115
 6120
 6125
 6130
 6135
 6140
 6145
 6150
 6155
 6160
 6165
 6170
 6175
 6180
 6185
 6190
 6195
 6200
 6205
 6210
 6215
 6220
 6225
 6230
 6235
 6240
 6245
 6250
 6255
 6260
 6265
 6270
 6275
 6280
 6285
 6290
 6295
 6300
 6305
 6310
 6315
 6320
 6325
 6330
 6335
 6340
 6345
 6350
 6355
 6360
 6365
 6370
 6375
 6380
 6385
 6390
 6395
 6400
 6405
 6410
 6415
 6420
 6425
 6430
 6435
 6440
 6445
 6450
 6455
 6460
 6465
 6470
 6475
 6480
 6485
 6490
 6495
 6500
 6505
 6510
 6515
 6520
 6525
 6530
 6535
 6540
 6545
 6550
 6555
 6560
 6565
 6570
 6575
 6580
 6585
 6590
 6595
 6600
 6605
 6610
 6615
 6620
 6625
 6630
 6635
 6640
 6645
 6650
 6655
 66

TABLE 3

Formulations	9	10	11	12	Control (#7)
Chlorinated Polyethylene, CPE (Tyrin 4211P)	28.6	39.3	39.3	39.3	33
Polyvinyl Chloride, PVC (Geon 179)	21.4	17.9	17.9	17.9	25
Santicizer 148	14.3	7.1	--	--	
Santicizer 141	--	--	7.1	--	
Santicizer 160	--	--	--	7.1	
Antimony Trioxide	5.7	5.7	5.7	5.7	7
Ammonium Polyphosphate (Phos-Chek P/40)	6.4	6.4	6.4	6.4	8
THOP Phosphite	0.7	0.7	0.7	0.7	1
Magnesium Oxide	2.9	2.9	2.9	2.9	3
Distearylthiodipropionate Antioxidant (DSTDP)	0.7	0.7	0.7	0.7	--
Irganox 1010 Antioxidant	--	--	--	--	1
Corn Starch	5.0	5.0	5.0	5.0	6
Hydrated Alumina	7.1	7.1	7.1	7.1	8
3/16" Glass Fiber	7.1	7.1	7.1	7.1	8
Properties					
Intumescence Efficiency (Highest Temperature °C)	320	325	342	351	301
Glass Transition (T _g °C) (Dynamic Measurement)	9	21	17	16	24
Tensile Strength (MPa)	2.25	2.94	3.29	2.80	13.0
Elongation at Break (%)	348	295	309	370	75
Tear Strength (kN/m)	21.1	26.1	25.6	23.6	49.0

As seen in the summary of properties included in the above Table 3, the addition of the respective plasticizer materials lowered the glass transition temperature as measured by a dynamic mechanical analyzer (DMA) from 24°C for the unplasticized control composition 7 to 9°C to 21°C to 17°C for the plasticized samples. The incorporation of the plasticizer contributed to an improvement in the ultimate elongation of samples 9 through 12 to values of 295 percent to 370 percent as compared with 75 percent ultimate elongation for the control sample. Improvements of this type in elongation can enable a particular part of the formulation to be made by vacuum forming or deep drawing. They also may provide improved impact resistance if that is required for a part application. On the other hand, as was expected, the incorporation of the plasticizers lowered the tensile strength of the compositions as compared to the control sample.

However, all of the plasticized samples 9 through 12 provided adequate protection against fire as measured by the intumescence efficiency procedure described above. The maximum temperatures for the plasticized samples were between 320°C and 351°C as compared to 301°C for the control sample.

It is recognized that molding compositions such as the subject materials must serve many different applications and situations and therefore must be capable of being formulated to provide a wide range of properties from the formulation family. In order to provide improvements in tensile strength while maintaining good low temperature properties, molding compositions may be employed in which the polyvinyl chloride hard polymer segment is replaced with other thermoplastic polymeric resins. Summarized in Table 4 below is composition 13 in which high density polyethylene (HXM50100, extrusion grade), a trademark of Phillips 66 Plastics, was included. The other constituents of the formulation are listed in Table 4 with the composition values in terms of parts or percentage by weight. Also included in Table 4 is the Intumescence Efficiency value measured on the molded slab of the composition and other relevant physical properties of the molded material. The high density polyethylene (HDPE), HXM 50100, is an example of an extrusion grade HDPE suitable for use in this invention. Phillips HMN 4550 is an example of a suitable injection molding grade HDPE for use in this invention.

TABLE 4

Formulations	13
Chlorinated Polyethylene, CPE (Tyrin 4211P)	33
High Density Polyethylene (HXM50100)	15.5
Chlorowax (Paroil 145)	8
Ammonium Dihydrogen Phosphate	16
Antimony Trioxide	4
DSTDP Antioxidant	0.5
Magnesium Oxide	4
Hydrated Aluminum Oxide	5
3/16" Glass	8
Corn Starch	3
Melamine	3
Properties	
Intumescence Efficiency (Highest Temperature °C)	314
Glass Transition (Tg °C)	11
Tensile Strength (MPa)	7.4
Elongation at Break (%)	474
Tear Strength (kN/m)	45

It is seen that composition 13 displayed a good Intumescence Efficiency of 314°C. This composition based on polyethylene demonstrated good low temperature behavior as well as high ultimate elongation.

In general, it is seen that a family of very useful moldable intumescent thermoplastic compositions can be based on chlorinated polyethylene and mixtures of chlorinated polyethylene with one or more of polyvinyl chloride and/or high density polyethylene. Each formulation contains suitable amounts of an intumescent additive and heat stabilizer along with optional additions of plasticizers, fillers, reinforcing agents and the like. In general, it is preferred that the amount of intumescent additive be in the range of about 25 to 40 percent by weight of the sum of the intumescent additive and the chlorinated polymer material. In general, it is also preferred that the amount of heat stabilizer lie in the range of about 5 to 15 percent by weight of the total of the heat stabilizer and chlorinated polymer material.

Because of their combination of good physical and intumescent properties, the subject moldings have utility as structural members, sound deadeners, heat barriers and other liner members over a broad range of temperatures.

While this invention has been described in terms of a preferred embodiment thereof, it will be appreciated that other forms could readily be adapted by one skilled in the art. Accordingly, the scope of this invention is to be considered limited only by the following claims.

Claims

1. An intumescent thermoplastic elastomer molding which is the molded product of a blended mixture initially comprising:

- (a) a moldable thermoplastic elastomer chlorinated polymer selected from the group consisting of chlorinated polyethylene elastomer and mixtures of 25 percent by weight or more of chlorinated polyethylene elastomer with at least one of polyvinyl chloride and high density polyethylene;
- (b) a heat stabilizer for the thermoplastic chlorinated polymer material; and
- (c) intumescent and fire-resistant additives for the chlorinated polymer material comprising,

(i) at least one constituent selected from the group consisting of hydrated alumina, hydrated magnesia and

melamine; and

(ii) at least one constituent selected from the group consisting of carbohydrates, trihydroxy alcohols and tetrahydroxy alcohols; and

(iii) at least one constituent selected from the group consisting of ammonium dihydrogen phosphate and ammonium polyphosphates;

said intumescent thermoplastic molding displaying a minimum tensile strength of 2.7 MPa (400 psi), a minimum elongation at break of 50 percent, and an Intumescence Efficiency of 450°C maximum as determined by the intumescent test procedure of this specification.

2. An intumescent thermoplastic molding as recited in claim 1 in which the intumescent additive is present in the blended mixture in an amount of about 25 percent by weight to 40 percent by weight of the total of intumescent additive and moldable chlorinated polymer.

3. An intumescent thermoplastic molding as recited in claim 1 in which the heat stabilizer is present in the blended mixture in an amount of about 5 to 15 percent by weight of the total of heat stabilizer and moldable chlorinated polymer.

4. An intumescent thermoplastic molding as recited in claim 1 in which the heat stabilizer is one or more materials selected from the group consisting of magnesium oxide, organic phosphite heat stabilizers, thio esters, hindered phenols, amine antioxidants and hydroquinone derivatives.

5. An intumescent thermoplastic elastomer molding which is the molded product of a blended mixture initially comprising:

(a) a moldable thermoplastic elastomer chlorinated polyethylene elastomer;

(b) a heat stabilizer for the thermoplastic chlorinated polyethylene elastomer, said heat stabilizer being present in the blended mixture in an amount of about 5 to 15 percent by weight of the total of heat stabilizer and chlorinated polyethylene; and

(c) intumescent and fire-resistant additives for the chlorinated polyethylene, said intumescent additive being present in the blended mixture in an amount of about 25 to 40 percent by weight of the total of the intumescent additive and chlorinated polyethylene and comprising,

(i) at least one constituent selected from the group consisting of hydrated alumina, hydrated magnesia and melamine; and

(ii) at least one constituent selected from the group consisting of carbohydrates, trihydroxy alcohols and tetrahydroxy alcohols; and

(iii) at least one constituent selected from the group consisting of ammonium dihydrogen phosphate and ammonium polyphosphates;

said intumescent thermoplastic molding displaying a minimum tensile strength of 2.7 MPa (400 psi), a minimum elongation at break of 50 percent and an Intumescence Efficiency of 450°C maximum as determined by the intumescent test procedure of the specification.

6. An intumescent thermoplastic elastomer molding which is the molded product of a blended mixture initially comprising:

(a) a moldable thermoplastic elastomer chlorinated polymer mixture consisting essentially of 25 to 74 percent by weight chlorinated polyethylene elastomer and the balance being at least one of polyvinyl chloride and high density polyethylene;

(b) a heat stabilizer for the thermoplastic chlorinated polymer mixture, said heat stabilizer being present in the blended mixture in an amount of about 5 to 15 percent by weight of the total of heat stabilizer and moldable chlorinated polymer mixture; and

(c) intumescent and fire-resistant additives for the chlorinated polymer mixture, said intumescent additive being present in the blended mixture in an amount of about 25 to 40 percent by weight of the total of the intumescent additive and moldable chlorinated polymer mixture and comprising,

(i) at least one constituent selected from the group consisting of hydrated alumina, hydrated magnesia and melamine; and

EP 0 761 755 A1

(ii) at least one constituent selected from the group consisting of carbohydrates, trihydroxy alcohols and tetrahydroxy alcohols; and

(iii) at least one constituent selected from the group consisting of ammonium dihydrogen phosphate and ammonium polyphosphates;

5

said intumescent thermoplastic molding displaying a minimum tensile strength of 2.7 MPa (400 psi), a minimum elongation at break of 50 percent and an Intumescence Efficiency of 360°C maximum as determined by the intumescent test procedure of the specification.

10

15

20

25

30

35

40

45

50

55

Fig.1.

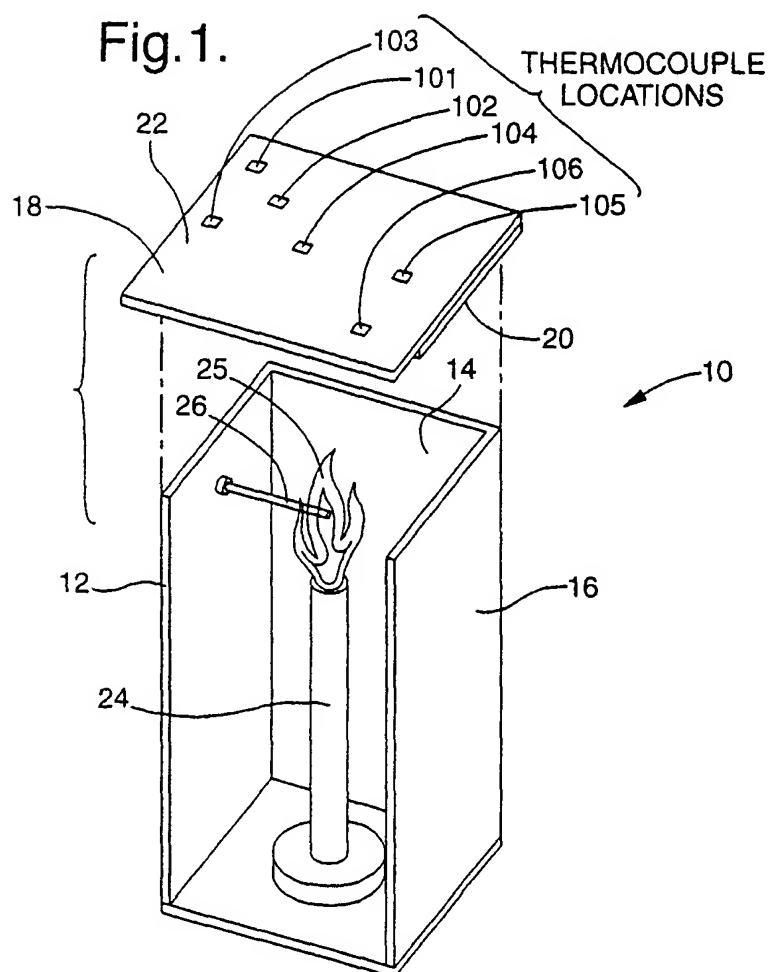


Fig.2.

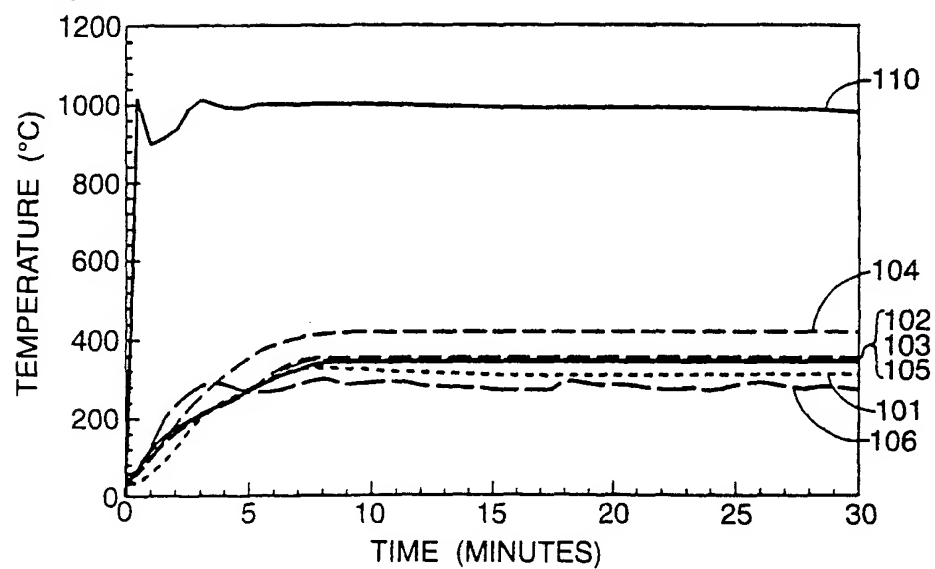


Fig.3.

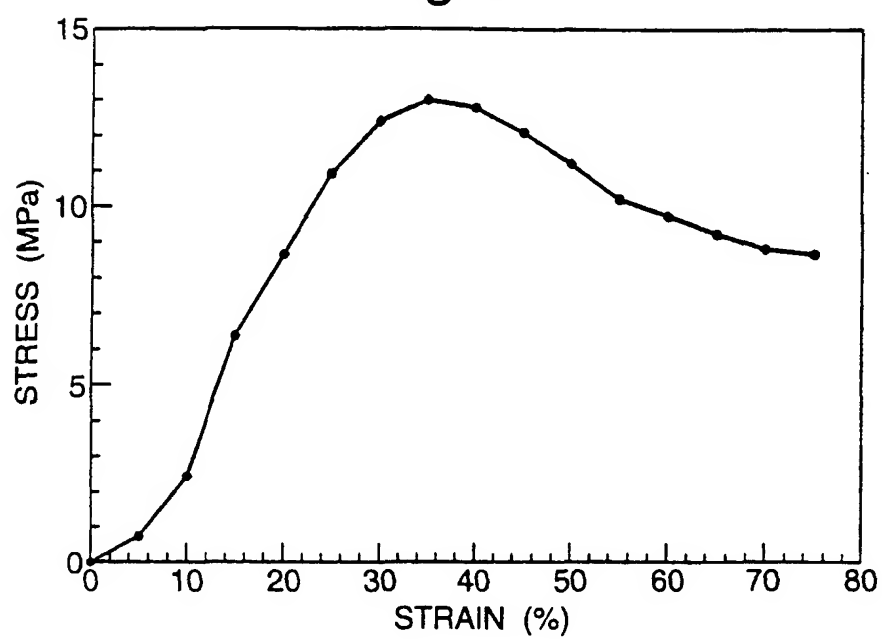
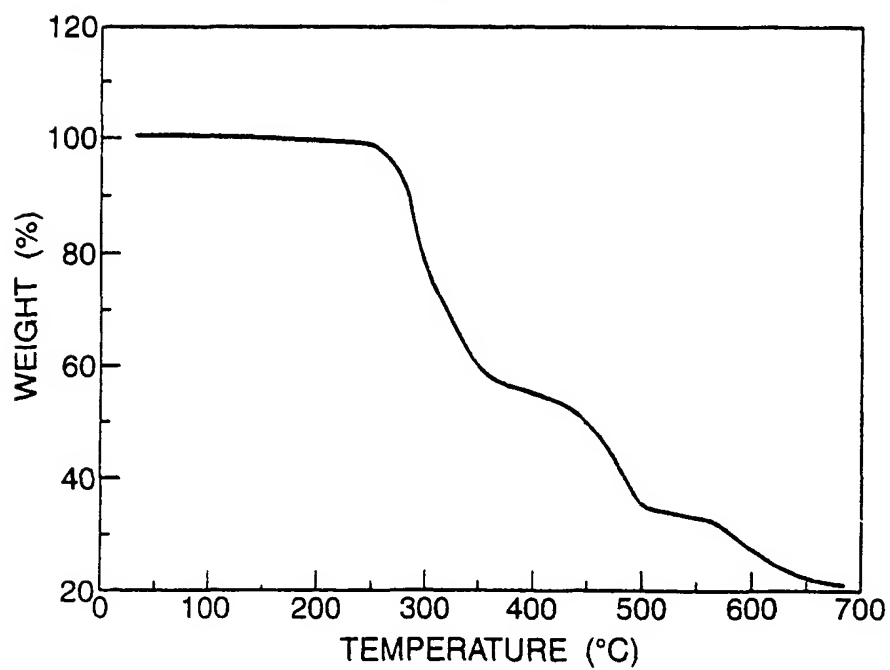


Fig.4.





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 20 1895

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	DATABASE WPI Week 8927 Derwent Publications Ltd., London, GB; AN 89-195718 XP002019067 & JP-A-01 132 685 (MITSUBISHI CABLE IND) * abstract * ---	1-6	C08L23/28 C09K21/14 C08K11/00
Y	DATABASE WPI Week 7818 Derwent Publications Ltd., London, GB; AN 78-32999a XP002019068 & JP-A-53 031 752 (SHOWA ELEC WIRE) * abstract * ---	1-6	
Y	FR-A-2 328 029 (SPIESS, HECKER) * the whole document * ---	1-6	
A	DD-A-153 210 (VEB LEUNA-WERK) * the whole document * ---	1,4	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP-A-0 167 084 (GEBRÜDER KÖMMERLING KUNSTSTOFFWERKE) * page 3, line 23 - page 5, line 20 * * page 10, line 11 - line 20 * ---	1,4,6	C09K C08L C08K
A	EP-A-0 111 287 (HOECHST AKTIENGESellschaft) * page 3, line 14 - page 5, line 15 * * page 5, line 25 - page 6, line 36 * * examples * ---	1,6	
A	US-A-4 129 535 (ELCIK) * column 2, line 3 - column 4, line 25 * * table 1 * -----	1,4,6	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		21 November 1996	Puetz, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 (12.92) (P04C01)